OFFICE OF NAVAL RESEARCH

Grant or Contract N00014-89-J-1590

R&T Code 413m012

Technical Report No. 2

Non-Destructive Characterization of Epoxy/Dicyandiamide
Interphases Using Surface-Enhanced Raman Scattering

by

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Prepared for Publication

in

Materials Science and Engineering

Department of Materials Science
and Engineering
University of Cincinnati
Cincinnati, OH   45221-0012

December 1, 1989

89 12 14

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS
None		None

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
None	This document has been approved for public release and sale; its distribution is unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
None	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report #2	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of Cincinnati		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Department of Materials Science Cincinnati, OH 45221-0012	800 North Quincy Street Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		N00014-89-J-1590

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
800 North Quincy Street Arlington, VA 22217	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Non-Destructive Characterization of Epoxy/Dicyandiamide Interphases Using Surface-Enhanced Raman Scattering

12. PERSONAL AUTHOR(S)
F. J. Boerio and P. P. Hong

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical Report	FROM _____ TO _____	December 1, 1989	31

16. SUPPLEMENTARY NOTATION
Prepared for publication in Materials Science and Engineering

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Surface-Enhanced Raman Scattering, Epoxy, Dicyandiamide, Interphases, Non-Destructive Characterization

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Surface-enhanced Raman scattering (SERS) is a process in which the Raman scattering cross section of molecules adsorbed onto the surfaces of metals such as silver, copper, and gold is increased by as much as six orders of magnitude compared to the cross section for normal Raman scattering from the bulk. However, the enhancement is short-range and is restricted to the first few layers of molecules adjacent to the surface. As a result, SERS can be used to characterize adsorption of organic compounds onto metals and can be used for non-destructive characterization of interphases between polymer films and metal substrates as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interphase. SERS spectra obtained from thin films of dicyandiamide (dicy) adsorbed from dilute solutions onto silver island films were characterized by very strong bands assigned to in-plane vibrations and very weak vibrations related to out-of-plane vibrations, indicating that dicy was adsorbed with a vertical configuration involving coordination through the nitrilo nitrogen atom. SERS spectra obtained from model adhesives consisting of 8:1 mixtures of digycidyl ether of bisphenol-A

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. Joann Milliken	(202)696-4410	

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

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August 15, 1989

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SUMMARY

Surface-enhanced Raman scattering (SERS) is a process in which the Raman scattering cross section of molecules adsorbed onto the surfaces of metals such as silver, copper, and gold is increased by as much as six orders of magnitude compared to the cross section for normal Raman scattering from the bulk. However, the enhancement is short-range and is restricted to the first few layers of molecules adjacent to the surface. As a result, SERS can be used to characterize adsorption of organic compounds onto metals and can be used for non-destructive characterization of interphases between polymer films and metal substrates as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interphase. SERS spectra obtained from thin films of dicyandiamide (dicy) adsorbed from dilute solutions onto silver island films were characterized by very strong bands assigned to in-plane vibrations and very weak vibrations related to out-of-plane vibrations, indicating that dicy was adsorbed with a vertical configuration involving coordination through the nitrilo nitrogen atom. The spectra obtained from model adhesives consisting of 8:1 mixtures of digycidyl ether of bisphenol-A (DGEBA) and dicy were identical to SERS spectra of dicy, indicating that dicy was preferentially adsorbed from the adhesive onto the silver surface and that the interphase in epoxy/dicy adhesives was likely to have composition that was enriched in dicy when compared to the bulk adhesive. Some evidence for adsorption of both DGEBA and dicy was observed in

SERS spectra obtained from 500:1 mixtures of DGEBA and dicy spin-coated onto silver island films from dilute solutions, indicating that in those cases there was insufficient dicyandiamide available to occupy all the SERS-active surface sites.

I. Introduction

Sharpe introduced the term "interphase" to describe the transition region between the adhesive and adherend in adhesive joints and between the fiber and matrix in composites in which the properties are different from those of either bulk material (1). The initial strength and durability of an adhesive joint or composite depend strongly on the molecular structure of the interphase. Therefore, control of the molecular structure of the interphase is essential in order to maximize the performance of an adhesive joint or a composite material in a given environment.

Despite the importance of interphases, there has been relatively little progress in determining their structure and properties because of the lack of suitable analytical techniques. In most cases, the interphase is present as a thin region between two relatively thick materials. In order to determine the properties of the interphase, the adhesive and substrate must usually be separated and surface analysis techniques used to characterize the failure surfaces.

We have been interested in determining the molecular structure of interphases for some time. In one investigation, we characterized the interphases formed when beams of epoxy resins were cured at elevated temperatures against metal beams that were pretreated with the silane coupling agent γ-aminopropyltrieth-oxysilane (γ-APS) (2). When the joints were cooled to room temperature after curing, the residual stresses were large enough that cracks could be propagated very near the interface. Analytical techniques such as x-ray photoelectron spectroscopy

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(XPS), internal reflection infrared spectroscopy (ATR), and external refelction infrared spectroscopy (RAIR) were then used to characterize the failure surfaces.

When a tertiary amine curing agent was used with the epoxy, there was little interdiffusion of the adhesive and the primer and a relatively sharp interphase was obtained (2). However, when an anhydride curing agent was used, there was a great deal of interdiffusion between the adhesive and the primer. The curing agent reacted with the primer to form an interphase containing amide and imide groups that were not found in the bulk of the adhesive. Some evidence for reaction of the anhydride curing agent with the oxide to form carboxylate species was also observed (2).

We also investigated the interphases formed when the epoxy/anhydride adhesive was cured against unprimed copper and 2024 aluminum substrates (3). It was found that the anhydride reacted with the cuprous oxide present on the surface of the copper substrates to form a relatively thick layer of carboxylate salts in the interphase. The anhydride adsorbed onto the Al_2O_3 on the surface of the 2024 aluminum substrates to form a type of surface complex but the reaction did not proceed beyond a monolayer. The copper alloying element was mostly present as an aluminide below the oxide and did not react with the anhydride.

Another approach to the characterization of polymer interphases is to sputter through one of the bulk materials and use surface analysis techniques such as XPS or Auger electron spectroscopy (AES) to characterize the interphase. Chaudhury (4)

used this approach to determine the structure of the interphase formed when a polyvinyl chloride plastisol was laminated against a germanium substrate that was pretreated with the silane coupling agent aminoethylaminopropyltriethoxysilane (AEAPS). It was found that interdiffusion of the silane and the plastisol was considerable when the primer was dried at $25^{\circ}C$ before the plastisol was applied. Much less interdiffusion was observed when the primer was dried at $175^{\circ}C$.

Relatively little progress has been made in the non-destructive characterization of polymer interphases. However, Garton (5) has used ATR to determine the structure of interphases in model graphite/epoxy composites by curing the composites directly in contact with an internal reflection crystal. In one experiment, polyacrylonitrile (PAN) was coated onto a germanium crystal and graphitized by heating in argon at $600^{\circ}C$. An epoxy was then cured against the coated crystal using an anhydride or amine curing agent and ATR infrared spectroscopy was used to characterize the "interphase." It was found that pretreating the graphite in a humid atmosphere resulted in a more rapid consumption of the anhydride curing agent, lower residual anhydride level, and a lower yield of ester products. Pretreating the graphite in the humid atmosphere had no effect on the polymerization reaction when the amine curing agent was used.

Although all of the techniques described above have been useful, there is still a great need for non-destructive techniques that can provide information regarding the molecular structure of polymer interphases. Recently, we have been

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interested in the use of surface-enhanced Raman scattering (SERS) for such purposes.

SERS is a process in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. However, the enhancement decreases very quickly as a function of distance and little enhancement is obtained for molecules that are more than a few monolayers away from the surface. As a result, SERS is surface selective. The scattering from a polymer film on a SERS-active substrate arises almost entirely from the first few molecular layers adjacent to the substrate as long as the film is less than approximately a thousand angstroms in thickness. Thus, SERS can be used for in-situ, non-destructive characterization of polymer interphases. Moreover, SERS can provide information regarding the composition and orientation of molecular species in the interphase.

Although many theories of SERS have been reported, it now appears that two mechanisms are responsible for most of the enhancement (6). One mechanism is associated with the large electric fields that can exist at the surfaces of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small (6). The other mechanism is related to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface (6). Enhancement due to the charge-transfer mechanism is restricted to the molecules

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immediately adjacent to the substrate but enhancement due to electromagnetic mechanisms may extend a few molecular layers away from the metal surface.

We have previously verified the surface-selectivity of SERS. In one case we investigated SERS from thin films of poly (α-methylstyrene) deposited onto silver island films (7). The intensity of the SERS spectra was independent of the thickness of the polymer films, indicating that SERS was an interfacial rather than bulk effect.

We also investigated SERS from bilayers prepared by depositing thin films of polymers such as polystyrene, poly (4-vinylpyridine), and the diglycidyl ether of bisphenol-A (DGEBA) onto silver island films and then overcoating them with much thicker films of polystyrene sulfonate (8). The SERS spectra were mostly characteristic of the polymers adjacent to the substrate. SERS was only observed from the overlayers when the first films were less than about a hundred angstroms in thickness.

In order to test the application of SERS to the analysis of polymer/metal interfaces, we considered the model anaerobic acrylic adhesive consisting of the monomer triethylene glycol dimethacrylate (TRIEGMA) and a redox cure system composed of acetylphenylhydrazine (APH), o-benzoic sulfimide (saccharin or BS), and cumene hydroperoxide (CHP) (9). This adhesive is known to cure rapidly in the absence of oxygen and in the presence of certain metals such as copper and iron. However, cure in the presence of other metals such as aluminum and zinc is much

slower. We were interested in determining how the cure rate was related to the interfacial chemistry.

SERS spectra were obtained from thin films spin-coated onto silver island films from the neat adhesive and from 1% and 5% solutions of the adhesive in acetone. There were several interesting aspects to the spectra. First, the spectra all had approximately the same intensity even though the films from which they were obtained had much different thicknesses, indicating that the observed SERS signal was characteristic of the interface and not of the bulk films. Moreover, the SERS spectra observed for the acrylic adhesive had little resemblance to normal Raman spectra of the monomer. Instead, they were similar to SERS spectra of saccharin and to normal Raman spectra of saccharin salts, indicating that saccharin in the adhesive segregated to the interface and adsorbed by dissociation to form a salt.

When saccharin was replaced in the adhesive with benzoic acid and the adhesive was spun onto a silver island film from a 1% solution in acetone, the SERS spectra obtained were virtually identical to SERS spectra of benzoic acid, indicating again that acidic compounds from the adhesive preferentially adsorbed onto the metal substrate by dissociation to form metal salts. Thus it was concluded that an interphase was formed that had composition that was considerably different from that in the bulk adhesive.

Recently, several papers have appeared which indicate that important interphases may be formed when epoxy adhesives containing the curing agent dicyandiamide are cured against metal substrates. Carter and coworkers reported that dicyandiamide was

reduced when heated against metallic zinc at 170°C for a few minutes but not when heated against steel or zinc oxide (10). Brockmann and coworkers (11) reported that dicyandiamide reacted with water to form guanylurea when heated at 120°C on the surface of anodic aluminum oxides.

Crompton used electron microscopy to observe two different interphases that were formed when a one-part epoxy was cured against aluminum at 180°C (12). One ("type B") extended as far as 1 μm from the substrate while the other ("type A") was restricted to approximately 10 nm from the substrate. Although Crompton did not identify the curing agent used in the adhesive, it was most likely dicyandiamide, which is widely used in one-part epoxies curing at 180°C.

The purpose of this paper is to describe the use of SERS for the non-destructive characterization of interphases between silver island films and a model epoxy adhesive system consisting of the diglycidyl ether of bisphenol-A and the curing agent dicyandiamide. The results obtained indicate that dicyandiamide is preferentially adsorbed from the epoxy adhesive onto the silver surface to form an interphase that has unique structure and properties. This interphase, which is formed within a few molecular layers of the substrate, may correspond to the "type A" interphase reported by Crompton (12). It has also been determined that dicyandiamide is adsorbed onto silver with a vertical conformation by coordination through the nitrilo nitrogen atom.

II. Experimental

Substrates for SERS were prepared by slow thermal evaporation of silver island films onto glass slides. In some cases, the slides were cleaned by immersion in a mixture of chromic and sulfuric acids for an hour, rinsed, and dried in nitrogen. In other cases, slides were cleaned by immersion in NaOH solutions for one hour, removed, rinsed in dilute hydrochloric acid solutions, and blown dry in a stream of nitrogen. Silver was evaporated onto the slides at a rate of about 1 A per second to a final thickness of about 45 A in a vacuum chamber equipped with sorption, sublimation, and ion pumps and a quartz crystal oscillator thickness monitor.

The diglycidyl ether of bisphenol-A (DGEBA) was obtained from Dow Chemical Co. and the curing agent dicyandiamide (dicy) was obtained from Aldrich Chemical Co. Both compounds were used as-received. Model adhesive systems were prepared by mixing DGEBA and dicy in the ratios 8:1 and 500:1 by weight. Samples were prepared for SERS by spin-coating thin films of dicy, DGEBA, and the adhesives onto silver island films from dilute solutions in HPLC grade dimethyformamide (Aldrich).

In order to estimate the thickness of the organic films on the SERS samples, thick films of aluminum were evaporated onto glass slides. Films of DGEBA, dicy, or the epoxy/dicy adhesives were spin-coated onto the aluminum substrates from the same solutions and at the same speeds as were used to prepare the SERS samples. The thickness of the organic films was determined by

using a Rudolph Research Model 436 ellipsometer to examine the aluminum films before and after deposition of the organic films.
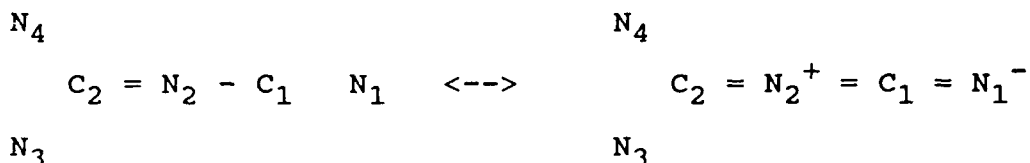
SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slits of the monochromator were set for a spectral resolution of 10 cm^{-1}. The laser beam was incident on the SERS samples at an angle of 65° relative to the normal to the sample surface and was polarized perpendicular to the plane of incidence. Scattered light was collected by an f/0.95 lens and focussed onto the entrance slit of the monochromator. Spectra were obtained using the 5145 A line of the laser, a scan rate of 50 cm^{-1}/min, and time constant of 10 sec.

Normal Raman spectra were obtained using the same instrument and techniques that have been described previously (13). The laser beam was focussed onto a small amount of powdered sample supported in a capillary tube and the scattered light was collected as described above. However, in this case the spectral slit width was about 2 cm^{-1}.

III. Results and Discussion

The normal Raman spectrum of dicyandiamide (dicy) was dominated by strong bands near 512, 532, 678, 944, and 2172 cm^{-1} and by weaker bands near 1108, 1536, 1556, 1650, and 2218 cm^{-1} (see Figure 1). Only one stretching mode related to the nitrile group was expected in the Raman spectra of dicyandiamide, near 2260-2240 cm^{-1} (14). However, two were observed, near 2172 and

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2218 cm^{-1}, indicating that a resonance effect occurred, weakening the C N bond

$$N_4 \qquad\qquad\qquad\qquad\qquad N_4$$
$$C_2 = N_2 - C_1 \quad N_1 \quad <\text{-->} \qquad C_2 = N_2{}^+ = C_1 = N_1{}^-$$
$$N_3 \qquad\qquad\qquad\qquad\qquad N_3$$

and lowering the frequency of the nitrile stretching vibration and causing it to split into two components. It is known from investigations of x-ray diffraction by dicy that the length of the C_1N_1 bond is around 1.22 A, which is longer than the bond length of the C N in CH_3CN (15).

Most of the remaining bands in the normal Raman spectra of dicy were interpreted using the assignments proposed by Jones and Orville-Thomas (16) for the bands observed in the infrared spectra. Thus, the bands near 512 and 532 cm^{-1} were assigned to $\gamma_r(N_3C_2N_4)$, an in-plane rocking mode, and $\beta(N_1C_1N_2)$, an out-of-plane bending mode, respectively. The strong band near 678 cm^{-1} was assigned to $\delta(N_3C_2N_4)$, an in-plane deformation mode. Bands near 944 and 1108 cm^{-1} were assigned to the symmetric stretching vibration $\nu_s(N_3C_2N_2)$ and to the NH_2 rocking mode $\gamma_r(NH_2)$, respectively. The pair of weak bands near 1536 and 1556 cm^{-1} was assigned to $\nu_a(N_3C_2N_2)$, an asymmetric stretching mode, and the broad, weak band near 1650 cm^{-1} was attributed to $\delta(NH_2)$, the in-plane deformation mode of the amino groups.

The SERS spectrum of dicyandiamide spin-coated from a 0.2 % solution in dimethylformamide onto a silver island film is shown in Figure 2. Strong bands were observed near 680, 941, 2182, and

2220 cm^{-1} and broad, weak bands were observed near 1105, 1350, and 1575 cm^{-1}.

The broad, weak bands near 1350 and 1575 cm^{-1} were attributed to graphite-like species formed by the decomposition of dicy or other organic species at the silver surface during intense laser irradiation. These bands have been observed in the SERS spectra of numerous compounds (7).

Several interesting differences were observed between the normal Raman and SERS spectra of dicy. The strong bands near 512 and 532 cm^{-1} in the normal Raman spectra of dicy were not observed in the SERS spectra. The strong band near 2172 cm^{-1} in normal Raman spectra shifted upward to about 2182 cm^{-1} in the SERS spectra while the weak band near 2218 cm^{-1} in normal Raman spectra increased greatly in intensity in the SERS spectra. The strong band near 944 cm^{-1} in normal Raman spectra was also strong in the SERS spectra but shifted downward slightly to 941 cm^{-1}.

There have been several papers describing complexes of dicyandiamide with metal ions (17-19). Monodentate complexes involving coordination through N_1 have been reported, as in $[Cd(dicy)_2I_2]$. Two different types of bidentate complexes involving coordination through N_1 and N_2 have been reported. In one type, such as $[Cd(dicy)(H_2O)_2(SO_4)_4]_2$, two dicy molecules act as bridges between two metal ions, resulting in formation of dimers. In the other type, one dicy molecule acts as a bridge between two metal ions, forming linear polymers as in $[Cd(dicy)Cl_2]$. The type of complex formed by dicy adsorbed onto silver can be determined by considering the relative intensities

of the bands observed in the SERS spectra and the theory of Raman scattering by molecules adsorbed at metal surfaces.

According to Moskovits, the strongest bands in the Raman spectra of molecules adsorbed onto metals are related to modes belonging to the same symmetry species as α_{zz}, where z is perpendicular to the surface of the metal, and having motions mostly perpendicular to the metal surface (20). The next strongest lines are those belonging to the same symmetry species as α_{xy} and α_{yz} while the weakest lines should be those belonging to the same symmetry species as α_{xx}, α_{yy}, and α_{xy}.

Dicyandiamide has a planar conformation in which the skeletal carbon and nitrogen atoms all lie in a plane while the hydrogen atoms in the amino groups lie nearly in the plane (19). The $N_1C_1N_2$ bond angle is about 175° but the other skeletal bond angles, such as $C_1N_2C_2$, $N_2C_2N_3$, $N_2C_2N_4$, and $N_3C_2N_4$ are approximately 120°. Accordingly, dicy has at most only two symmetry elements, the identity operation and a plane of reflection, and belongs to the point group C_s. In-plane vibrations belong to the symmetry species A′ and out-of-plane vibrations belong to A′′. If the z axis is in the plane of the molecule, α_{zz} also belongs to the A′ species.

Assuming that dicy was adsorbed onto the silver surface with a vertical conformation in which N_1 was in contact with the surface, the strongest bands in the SERS spectra should be associated with those in-plane stretching and bending modes of the molecular skeleton having displacements mostly perpendicular to the surface. The out-of-plane modes should be weak. If dicy

was adsorbed with a bidentate structure, the C_1N_1 and C_1N_2 bonds would be parallel to the surface. The displacements associated with out-of-plane modes and certain in-plane modes such as $\nu_a(N_1C_1N_2)$ and $\nu_s(N_2C_2N_3)$ would be parallel to the surface and the corresponding bands would be weak.

Reference to Figure 2 indicates that the strongest bands in the SERS spectra of dicy are those near 2182 and 2220 cm^{-1} associated with $\nu_a(N_1C_1N_2)$ and near 941 cm^{-1} associated with $\nu_s(N_2C_2N_3)$. These modes both belong to the species A', as does α_{zz}, and involve displacements that are approximately parallel to the N_1C_1 and C_1N_2 bonds. The strong band near 532 cm^{-1} in normal Raman spectra of dicy which is assigned to the out-of-plane mode $\beta(N_1C_1N_2)$ belonging to the species A'' is not observed in SERS spectra. Therefore, it is clear from the SERS spectra that dicy is adsorbed onto the silver surface with a vertical conformation and that coordination is through N_1.

Hubbersty (18) has pointed out that there is not a single vibrational mode in dicy that is characteristic of the mode of coordination. Nevertheless, Colthup has pointed out that the frequency of the nitrilo stretching mode increases upon coordination through the nitrilo nitrogen atom (22) and Hubbersty has observed that the frequency of $\nu_a(N_1C_1N_2)$ increases more during monodentate coordination of dicy through N_1 than it does upon bidentate coordination through N_1 and N_2 (18). We observed that the bands assigned to $\nu_a(N_1C_1N_2)$ were shifted to higher frequencies in the SERS spectra of dicy than in the normal Raman

spectra, perhaps providing more evidence for coordination through the nitrilo nitrogen atom.

The SERS spectra shown in Figure 3 were obtained from a sample that was prepared by spin-coating dicy onto a silver island film from a 0.2 % solution in dimethylformamide and then spinning a much thicker film of epoxy onto the same silver island film from a 3 % solution in toluene. These spectra were virtually identical to SERS spectra of dicy alone (see Figure 2), and indicated that SERS could be used to detect preferential adsorption of dicy from an adhesive onto the silver surface.

SERS spectra were obtained from a sample prepared by spin-coating a 3 % solution of an 8:1 mixture of epoxy and dicy onto a silver island film (see Figure 4A). Bands characteristic of dicy were observed near 680 and 940 cm^{-1} but no bands related to the epoxy were observed, indicating that dicyandiamide had preferentially adsorbed onto the silver substrate. Bands characteristic of graphitic species were also observed near 1350 and 1575 cm^{-1}. Nearly identical SERS spectra were obtained from samples prepared by spin-coating films from 10 % and 60 % solutions of the same 8:1 mixture of epoxy and dicy onto silver island films (see Figures 4B and 4C). The appearance and intensity of the SERS spectra did not depend on the concentration of the solutions even though the thickness of the films deposited onto the silver island films varied from approximately 10 nm for the 3 % solution to 150 nm for the 60 % solution. Thus, it was evident that the spectra were characteristic of the interphase

between the adhesive and the silver and not the bulk of the adhesive.

SERS spectra were also obtained from a thin film spin-coated onto a silver island film from a dilute solution of a 500:1 mixture of epoxy and dicy (see Figure 5). Bands characteristic of dicyandiamide were observed near 680 and 940 cm^{-1} in both of these SERS spectra. However, bands related to the epoxy were also observed near 840, 1120, and 1610 cm^{-1}. These results indicate that the concentration of dicyandiamide in the mixture was too small to occupy all the SERS-active sites on the surface and that some of the sites were occupied by the epoxy.

It is interesting to note that the bands related to dicyandiamide were observed in the SERS spectra shown in Figure 5 even though there was 500 times as much epoxy as dicyandiamide in the solution used to prepare the specimen. This indicates once again that dicy was preferentially adsorbed onto the silver substrate and that the SERS spectra were characteristic of the interphase rather than the bulk of the adhesive.

As indicated above, Carter et al reported that dicy was reduced when thin films were applied to metallic zinc and heated to 170°C but not when similar experiments were carried out using steel substrates (10). Brockmann et al (11) suggested that dicy reacted with water to form guanylurea when heated at 120°C on the surface of anodic oxides on aluminum. We investigated possible reactions of dicy on silver surfaces using SERS. However, when silver island films were heated to temperatures near 170°C, the morphology was altered and no SERS spectra could be obtained.

Experiments were also carried out using reflection-absorption infrared spectroscopy to investigate reactions of thin dicy films spin-coated onto thick evaporated silver films but no evidence for reaction of dicy was observed after heating at 170°C.

It is interesting to compare the results obtained here with those reported by Crompton (11). The interphase adjacent to the silver which is substantially enriched in dicyandiamide may correspond to the "type A" interphase which Crompton observed within 10 nm of the substrate when an epoxy was cured against aluminum using dicyandiamide as the curing agent. In that case, it may be speculated that the "type B" interphase observed by Crompton may correspond to a region in which dicyandiamide was depleted. More work which is intended to clarify these points is in progress.

IV. Conclusions

In surface-enhanced Raman scattering, the Raman scattering cross section of molecules adsorbed at the surfaces of metals such as silver, gold, and copper is increased by up to 10^6. However, the enhancement is confined to the first few adsorbed layers. SERS can, therefore, be used for the non-destructive characterization of interfaces between polymer films and metals as long as the thickness of the polymer films is not so great that normal Raman scattering by the bulk films is comparable in intensity to the SERS from the interface. The thickness of polymer film at which that happens depends on the Raman cross section of the polymer and we have not carried out careful

determinations. However, present results indicate that films as thick as about 1,000 A can be examined.

Several differences were observed between normal Raman and SERS spectra of dicyandiamide spin-coated onto silver island films from dilute solutions. Bands near 512 and 532 cm^{-1} in normal Raman spectra of dicy were very weak in SERS spectra. A band assigned to the C N stretching mode was observed near 2218 cm^{-1} in the normal spectra but shifted upward in frequency by about 2 cm^{-1} in the SERS spectra and increased greatly in intensity. Another band assigned to the C N stretching mode was observed near 2172 cm^{-1} in normal Raman spectra but shifted upward to near 2182 cm^{-1} in SERS spectra. These changes in the Raman spectra indicated that dicy was adsorbed onto silver island films with a vertical conformation in which the nitrilo nitrogen atoms were in contact with the surface.

SERS spectra obtained from mixtures of epoxy resins and dicyandiamide spin-coated onto silver island films from solution were independent of thickness, indicating that the spectra were characteristic of the adhesive/substrate interphase rather than the bulk of the adhesive. SERS spectra of epoxy/dicy mixtures were similar to SERS spectra of dicy itself, indicating that dicy was preferentially adsorbed onto the silver surface to form an interphase that was relatively rich in curing agent and that the state of cure and the physical properties in the interphase are different than in the bulk of the adhesive. No reactions were observed when dicy was heated against silver at 170°C.

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V. Acknowledgements

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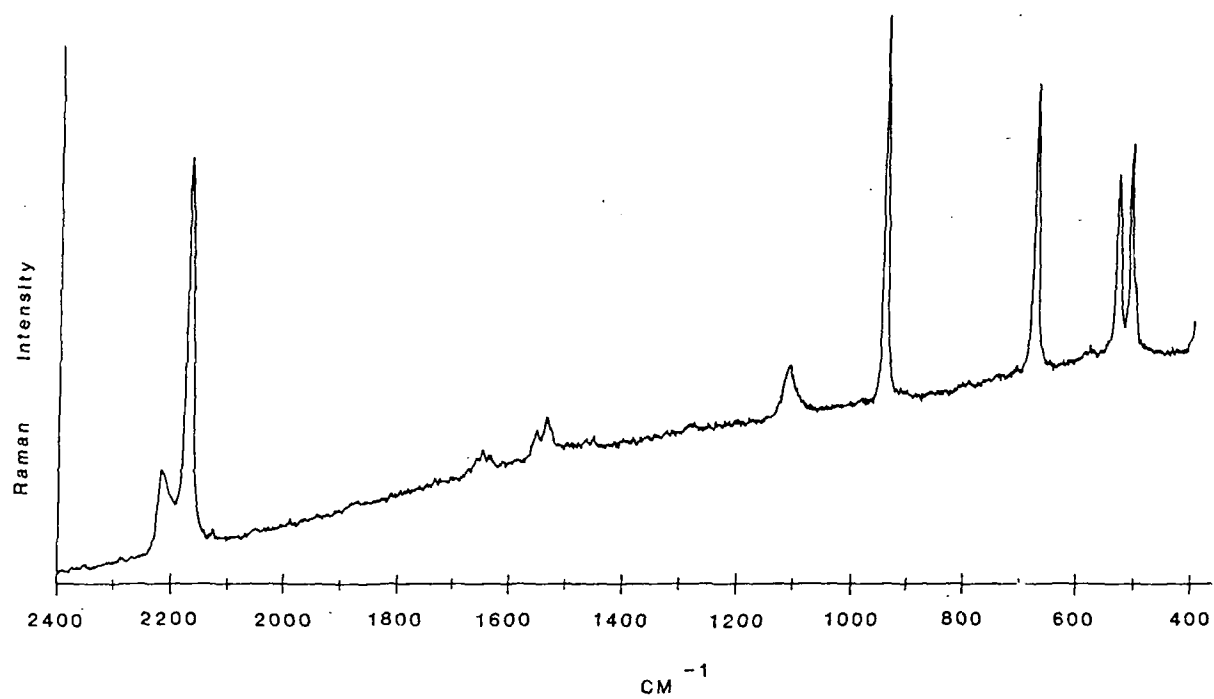
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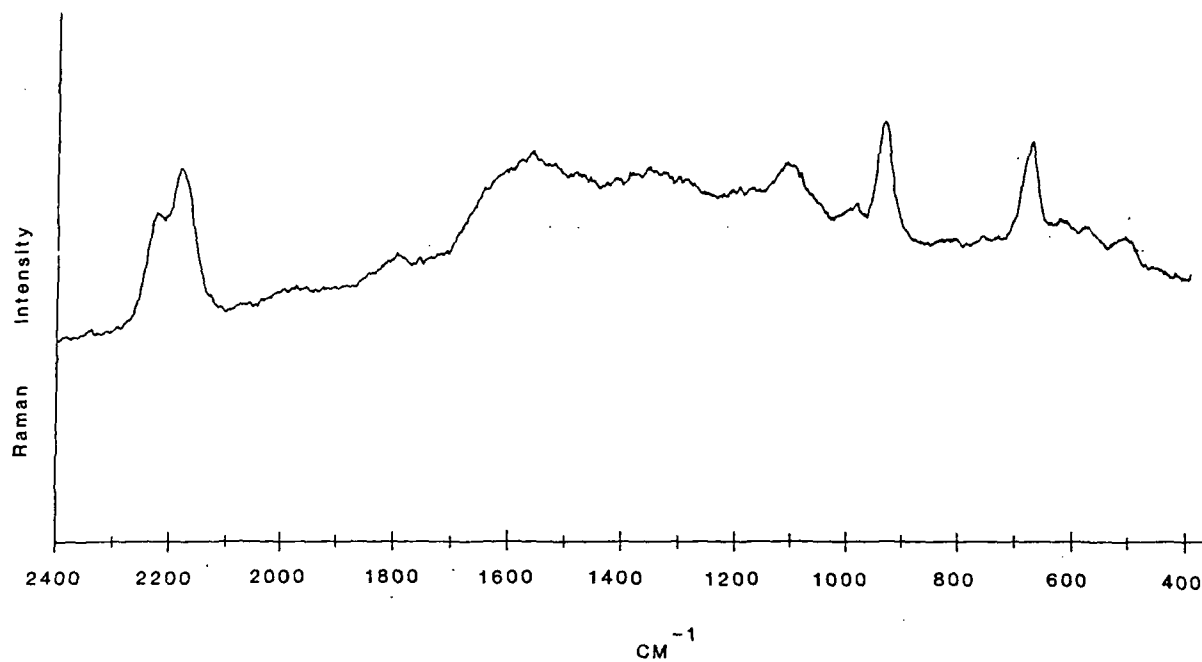Figure 1. Normal Raman spectrum of dicyandiamide.

Figure 2. Surface-enhanced Raman spectrum of dicyandiamide spin-coated onto a silver island film from a dilute solution in dimethylformamide.
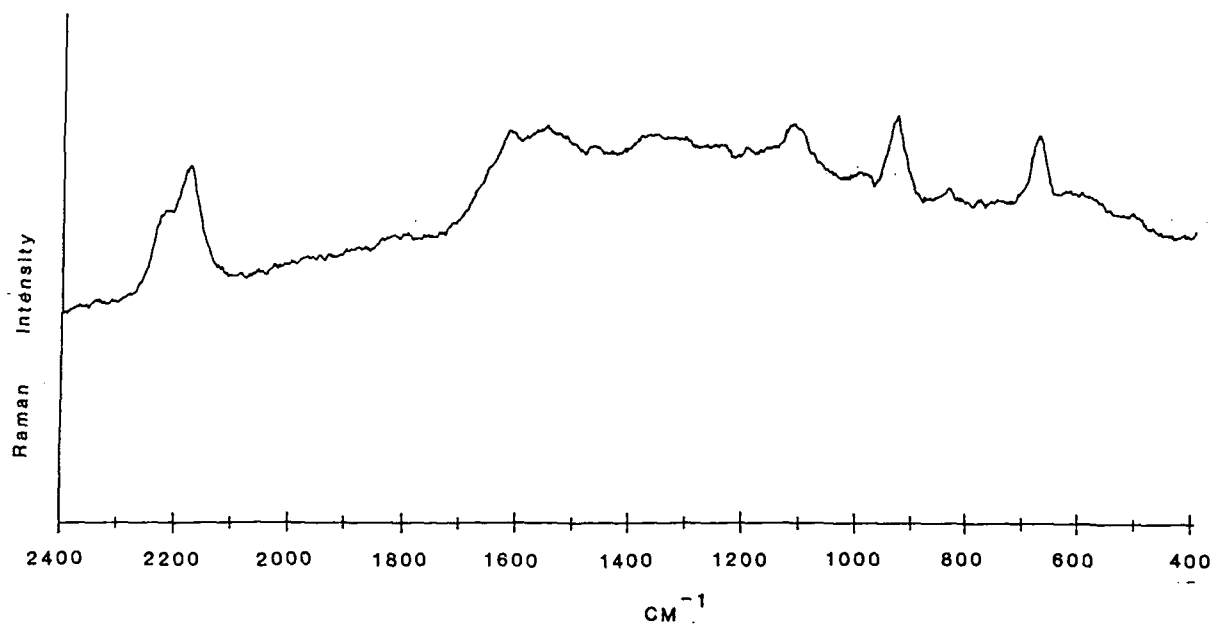
Figure 3.   SERS spectrum obtained after a thin film of
            dicyandiamide was spin-coated onto a silver island
            film from a 0.2% solution in dimethylformamide and
            then overcoated with a thicker film of DGEBA spun from
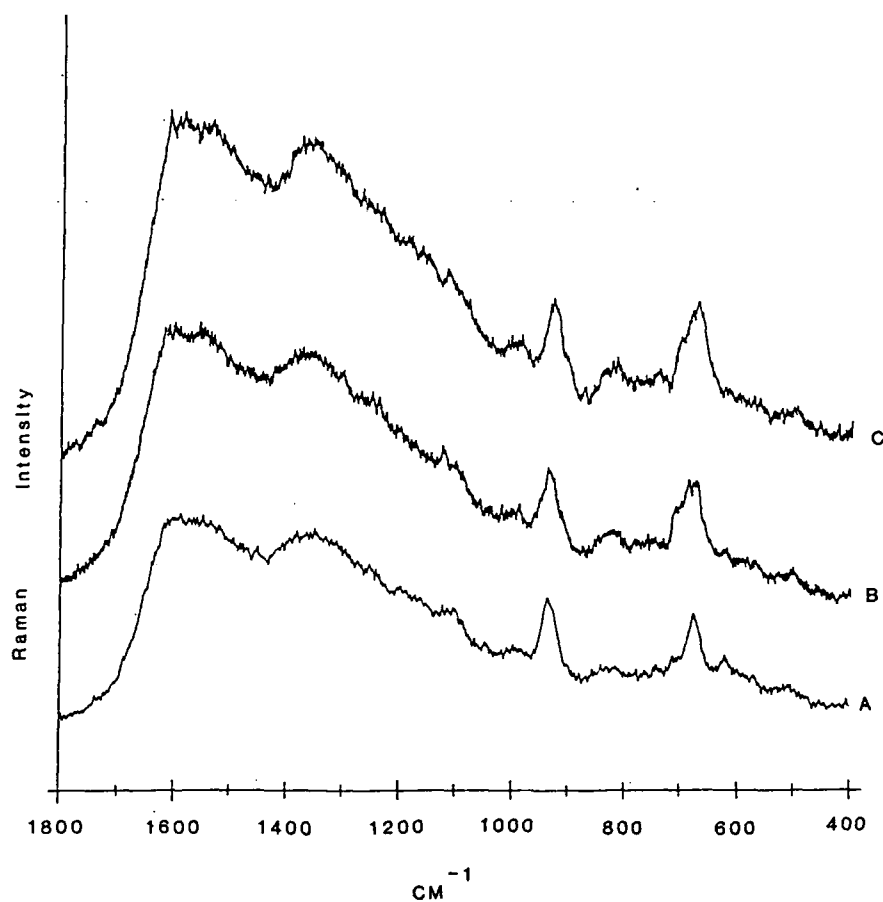   a 3% solution in toluene.

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Figure 4. SERS spectra obtained after an 8:1 mixture of DGEBA and dicyandiamide was spin-coated onto silver island films from (A)-3%, (B)-10%, and (C)-60% solutions in dimethylformamide. The thickness of the films ranged from approximately 10 nm in (A) to 150 nm in (C).
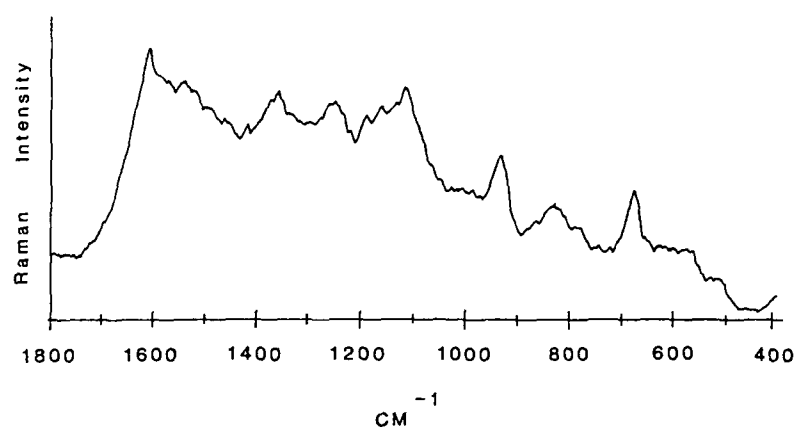
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Figure 5.   SERS spectra obtained after a 500:1 mixture of DGEBA
and dicyandiamide was spin-coated onto a silver island
film from a dilute solution in dimethylformamide.

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